

TRANSLATION

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the zinc oxide system porcelain laminated material for zinc oxide varistors used for absorption of the surge generated all over an electrical circuit etc., its manufacture approach, and a zinc oxide varistor.

[0002]

[Description of the Prior Art] Making a varistor property produce, the latter surface barrier mold zinc oxide varistor contacts the front face of a zinc oxide subject's sintered compact in a metal, and makes the barrier of a shot key mold roughly divide into a zinc oxide varistor and there be two kinds, a grain boundary barrier mold and a surface barrier mold, and the former grain boundary barrier mold zinc oxide varistor form the barrier which adjusts the flow of a current in the so-called grain boundary between the zinc oxide particle which constitutes a zinc oxide subject's sintered compact, and a zinc oxide particle, and form in it on the surface of a sintered compact.

[0003] The former grain boundary barrier mold zinc oxide varistors are ZnO and a basic additive. Bi<sub>2</sub>O<sub>3</sub> and MnO. It reaches. CoO, In the sintered compact of the zinc-oxide system porcelain which is manufactured using the zinc-oxide system porcelain obtained by casting and calcinating the zinc-oxide raw material powder containing various kinds of oxides furthermore added for the improvement in the engine performance and which was. Hidden and manufactured A depletion layer is formed in the interior of each zinc-oxide particle of both sides along the grain boundary of the zinc-oxide particle to constitute. by which the barrier of the shot key mold which prevents a current is formed in a grain boundary. said to form the barrier of a double shot key mold since the barrier of a shot key mold is formed in the both sides of this field granulation community Since this barrier exists It is. [0004] by which a current does not flow in the beginning even if it forms an electrode in zinc oxide system porcelain and carries out the seal of approval of the electrical potential difference to it, but an electrical potential difference is called voltage at reference current and in which a current will begin to flow rapidly if it starts and an electrical potential difference is reached, and the so-called varistor property appears. The standup electrical potential difference of a grain boundary barrier mold zinc oxide varistor In order to manufacture the zinc oxide varistor for about [ 300V ] high tensions per [ by which going up in proportion / almost / to the number of the grain boundaries which exist in inter-electrode / of a component / is known ] mm in thickness., then conventionally [ with required manufacturing the sintered compact which has a ZnO particle with a small particle size with a mean particle diameter of about 10 micrometers ] .Sb<sub>2</sub>O<sub>3</sub> for which the approach of controlling growth of a ZnO particle by adding the grain growth retardant of ZnO particles, such as Sb<sub>2</sub>O<sub>3</sub>, has been used in order to manufacture the zinc oxide varistor for high tensions also performs important work of stabilizing the nonlinear resistive characteristic of a zinc oxide varistor. grain boundary barrier mold zinc oxide varistor. with required manufacturing the sintered compact which has a ZnO particle with a large particle size with a mean particle diameter of about 150 micrometers, in order to manufacture the zinc oxide varistor for low batteries of an about [ 20V ] standup electrical potential difference per mm in thickness -- in order to manufacture the zinc oxide

varistor for low batteries conventionally, the method of aiming at growth of a ZnO particle has been used by adding the grain growth promotor of ZnO particles, such as TiO<sub>2</sub>, there

[0005] In addition, start and an electrical potential difference means the electrical potential difference between the ends children when usually passing a 1mA current to a varistor. The electrical potential difference between the ends children when passing a 1mA current in the sample whose thickness is 1mm in the grain boundary barrier mold zinc oxide varistor of . former expressed with V1mA is set to one of the constants of this ingredient. . which may be expressed with V1mA/mm -- the electrical property of . zinc oxide varistor which this will call the standup electrical potential difference per thickness of 1mm of samples often -- a previous standup electrical potential difference and nonlinear resistance characteristic  $I=(V/V_0)^\alpha$  expressed with a degree type using alpha -- here I The current which flows a component V . showing the electrical potential difference by which the seal of approval was carried out among the ends children of a component V<sub>0</sub> . which is a constant -- in addition in a zinc oxide varistor, the electrical property is excellent -- for example, the leakage current -- few -- nonlinear resistance characteristic alpha is with a high property etc. Moreover, when a long duration power load is added under an elevated temperature, and a high current pulse is impressed further, there is no lowering of an electrical property etc. and most of the . current to which the matter of the electrical property of a basis being maintained is mentioned, and the zinc oxide varistors which have come out to the commercial scene belong [ when a long duration electrical potential difference is impressed as dependability is excellent, or ] to the former grain boundary barrier mold zinc oxide varistor.

[0006] On the other hand, the latter surface barrier mold zinc oxide varistor Apply metal pastes, such as silver containing a glass frit etc., to the front face of a zinc-oxide subject's sintered compact, and a depletion layer is formed in the interior of a zinc-oxide sintered compact along the front face of a subject's sintered compact in the zinc-oxide varistor which is heat-treated and manufactured and which was. Hidden and manufactured. . by which the barrier of the shot key mold which prevents a current is formed in a zinc oxide sintered compact front face, since this barrier exists Even if it forms an electrode in other one side of a sintered compact and carries out the seal of approval of the electrical potential difference, a current does not flow in the beginning. if an electrical potential difference reaches the standup electrical potential difference called voltage at reference current, a current will begin to flow rapidly, since the barrier of a shot key mold comes out further and there is in . surface barrier mold zinc oxide varistor by which the so-called varistor property appears, it starts, and an electrical potential difference becomes settled mostly. When it starts and an electrical potential difference arrives at about 1V, when a current flows toward a zinc-oxide sintered compact from a metal-electrode side in the part of the barrier (forward direction), and a current flows toward a metal electrode from a zinc-oxide sintered compact side (hard flow), it starts and an electrical potential difference takes an about [ 3V ] value.

[0007]

[Problem(s) to be Solved by the Invention] . from which the noise of a high frequency occurs, it becomes the cause of a trouble variously, and clearance of the noise of a high frequency serves as pressing need with the digitized various electronic instruments if digitization of an electronic circuitry progresses in recent years The conventional grain boundary barrier mold zinc oxide varistor has the outstanding surge absorption property, and has been used as a surge suppressor by the object of small size as an arrester in a power-transmission-and-distribution circuit by the thing of large size in the electronic circuitry. However, in these zinc oxide varistors, since the electrostatic capacity was large, the noise of a high frequency could not be absorbed, but utilization of the zinc oxide varistor of the high performance for high frequency with small electrostatic capacity was desired. In the circuit especially using a semi-conductor, it starts and the varistor for low batteries 10 volts or less is called for for an electrical potential difference.

[0008] At a grain boundary barrier mold zinc oxide varistor, the standup electrical potential difference as a varistor is . decided by the number of the inter-electrode grain boundaries of a component. In the sintered compact of a zinc oxide varistor The standup electrical potential difference of a between [ a zinc-oxide crystal and zinc-oxide crystals (i.e., one grain boundary) ] is abbreviation. If it is going to obtain the varistor for low batteries not more than .10 volt which is 3.0-3.3 volts Bi<sub>2</sub>O<sub>3</sub> which promotes

liquid phase sintering in the grain boundary of . zinc oxide varistor for which it is necessary for the number of grain boundaries to attach an electrode to 1-3 sintered compacts, . by which the existence of CoO and MnO which carries out the trap of the electron has been needed for a grain boundary in order to form a depletion layer in a zinc-oxide particle along a grain boundary In order to acquire the stability as a varistor further Existence of Sb 2O<sub>3</sub> was indispensable again because of the improvement in non-linear characteristics.,

[0009] Since 2OZnO-Bi<sub>3</sub> system which is the basic presentation of the porcelain of a zinc oxide varistor has the eutectic presentation with the eutectic temperature of 740 degrees C, these two persons of ZnO and Bi 2O<sub>3</sub> react easily also in the temperature of about 800 degrees C. However, this reaction will be barred if Sb 2O<sub>3</sub> exists here. if Sb 2O<sub>3</sub> becomes hundreds of times -- sublimating -- a zinc-oxide front face -- covering -- Sb2O<sub>3</sub> themselves -- or the compound of ZnO and Sb 2O<sub>3</sub> bars contact between two persons of the above Bi [ ZnO and ] 2O<sub>3</sub>. When . in which Sb 2O<sub>3</sub> may react to with ZnO first, and may furthermore form the pyrochlore phase of stable solid phase chemically in response to a degree with Bi 2O<sub>3</sub>, therefore Sb 2O<sub>3</sub> are added, in order to acquire the outstanding varistor property It was required to calcinate by high temperature 1200 degrees C or more.

[0010] . from which the varistor which was excellent also in baking with a low temperature of 850-950 degrees C when there is progress of a manufacturing technology, Sb 2O<sub>3</sub> and Bi2O<sub>3</sub> were made to react beforehand and this was added to ZnO with other additives in recent years came to be obtained With these new techniques, versatility, The varistor for low batteries with the high dependability whose standup electrical potential difference is about 20V is developed. A nonlinear resistance characteristic alpha value by 20-30 1000 Amp/cm<sup>2</sup> To (8x20microsec) . by which the \*\*\*\*\* thing is also developed, however the zinc oxide varistor for these low batteries are . which electrostatic capacity was not able to use for absorption of the noise of high frequency etc. greatly. Although the standup electrical potential difference of a grain boundary barrier mold zinc oxide varistor is decided by the number of the grain boundaries which exist in inter-electrode [ of a component ] mostly The electrostatic capacity of a component becomes large in proportion to an electrode surface product like the case of a capacitor, and is in inverse proportion to the thickness of an inter-electrode insulating layer. Therefore, it starts, and with a component with a low electrical potential difference, since there are few grain boundaries simultaneously, electrostatic capacity is large. When an electrode diameter was the practical zinc oxide varistor of the disk mold which is 10mm, although the standup electrical potential difference was low made to about about ten volts, if the electrostatic capacity at that time tends to start to . pan used as the value before and behind 10nF(s) and tends to make an electrical potential difference low, or when it was going to make the electrode surface product small, dispersion in a standup electrical potential difference or electrostatic capacity became large rapidly, and production became difficult. The grain boundary formed of . sintering which was stabilized and was not able to manufacture the zinc oxide varistor for low batteries of low electrostatic capacity excellent in an electrical property and dependability by the creation approach of the conventional ZnO sintered compact as mentioned above was what was produced spontaneously, and it was difficult to obtain the sintered compact which controls a grain boundary in the conventional sintering process, and has one layer or the two-layer barrier.

[0011] . to which the experiment which forms a micro electrode on one field of the sintered compact of a zinc oxide varistor, and searches for the current-voltage characteristic in order to know the standup electrical potential difference per grain boundary in the conventional grain boundary barrier mold zinc oxide varistor was reported -- that is, On one field of the sintered compact of a zinc oxide varistor, attach a metal membrane and a micro electrode is formed suitably, making full use of techniques, such as etching. . which was asking for the relation between the number of 2 inter-electrode grain boundaries, and the current-voltage characteristic -- consequently As described previously, it depends and starts to one zinc oxide grain boundary, and an electrical potential difference is about 3.0-3.3 volts. Although . by which what was excellent in the nonlinear resistive characteristic was observed, however these showed the varistor property, dispersion in data was large, the property was unstable, and it was impossible to have used it as a practical use component.

[0012] In one side Thin films, such as bisumuth oxide, are formed on a zinc oxide single crystal. A

direct electrode is formed on it or a zinc-oxide thin film is formed. Attach an electrode on it or Or . by which the efforts for for obtaining the varistor which heat-treats to the whole on both sides of the bisumuth-oxide film with a zinc oxide single crystal, and has one grain boundary have been made, however the obtained thing have an unstable electrical property. . which was difficult for a nonlinear resistive characteristic not being excellent furthermore and using it as a component -- this is because the grain boundary equivalent to the grain boundary of the grain boundary barrier mold zinc oxide varistor put in practical use is not formed in what was used for these experiments.

[0013] In a surface barrier mold zinc oxide varistor, improvement in a property of the varistor by the combination of the sintered compact of a zinc oxide principal component and silver electrode containing various additives has been achieved. However, compared with the grain boundary barrier mold zinc oxide varistor, the variation in an electrical potential difference is large, and the conventional surface barrier mold zinc oxide varistor had the quite low stability over the seal of approval of a pulse again. Although stability increased so much to the seal of approval of a pulse when it could be burned and temperature was especially made high, the variation in an electrical potential difference became large. Although the surface barrier mold zinc oxide varistor started and the electrical potential difference had turned to the varistor for low batteries low, utilization was difficult at the variation in an electrical potential difference, the stability over a pulse seal of approval, etc.

[0014] In order that this invention may solve the above-mentioned conventional problem, . aiming at offering the zinc oxide system porcelain laminated material and its manufacture approach for manufacturing the zinc oxide varistor of the low battery of low electrostatic capacity excellent in electrical properties, such as a nonlinear resistive characteristic with one pair of barrier layers, by the high yield -- and It aims at offering the zinc oxide system porcelain laminated material and its manufacture approach for multiplexing this and manufacturing the zinc oxide varistor of a necessary standup electrical potential difference or electrostatic capacity by the high yield.

[0015]

[Means for Solving the Problem] In order to attain said object, the zinc-oxide system porcelain laminated material of this invention On the field of the zinc-oxide system porcelain containing MnO, CoO, Fe 2O<sub>3</sub>, NiO and MgO, aluminum2O<sub>3</sub>, and at least one oxide in BeO Bi 2O<sub>3</sub>, Sb2O<sub>3</sub>, B-2s Cr [ O<sub>3</sub> and ] 2O<sub>3</sub>, PbO, TiO<sub>2</sub>, SiO<sub>2</sub>, SnO<sub>2</sub> and Ta 2O<sub>5</sub>, GeO<sub>2</sub>, BaO, It has the configuration of coming to carry out the laminating of said zinc-oxide system porcelain and the zinc-oxide system porcelain of the same kind through the oxide film containing SrO, Y2O<sub>3</sub>, Pr2O<sub>3</sub>, and at least two oxides in CoO and MnO.

[0016] In the above-mentioned zinc-oxide system porcelain laminated material the oxide film Moreover, Bi 2O<sub>3</sub>, Sb2O<sub>3</sub>, B-2 O<sub>3</sub>, Cr2O<sub>3</sub>, PbO, TiO<sub>2</sub>, SiO<sub>2</sub>, SnO<sub>2</sub>, Ta 2O<sub>5</sub>, GeO<sub>2</sub>, BaO, SrO, It has the configuration of consisting of oxide film containing the artificial oxides which heat-treated the range of 350 degrees C - 700 degrees C into the mixture which consists of Y2O<sub>3</sub>, Pr2O<sub>3</sub>, and at least two oxides in CoO and MnO, and were obtained into it.

[0017] In order to attain said object, moreover, the zinc-oxide system porcelain laminated material of this invention On the field of the zinc-oxide system porcelain containing MnO, CoO, Fe 2O<sub>3</sub>, NiO and MgO, aluminum2O<sub>3</sub>, and at least one oxide in BeO, to two places Bi 2O<sub>3</sub>, Sb2O<sub>3</sub>, B-2s Cr [ O<sub>3</sub> and ] 2O<sub>3</sub>, PbO, TiO<sub>2</sub>, SiO<sub>2</sub>, SnO<sub>2</sub> and Ta 2O<sub>5</sub>, GeO<sub>2</sub>, BaO, It has the configuration of coming to carry out the laminating of said zinc-oxide system porcelain and the zinc-oxide system porcelain of the same kind through the oxide film containing SrO, Y2O<sub>3</sub>, Pr2O<sub>3</sub>, and at least two oxides in CoO and MnO.

[0018] Moreover, in the above-mentioned zinc-oxide system porcelain laminated material, on the field of zinc-oxide system porcelain, two places are equipped with the configuration that it is the field where said zinc-oxide system porcelain differed, and set to the further above-mentioned zinc-oxide system porcelain laminated material. The oxide film Bi 2O<sub>3</sub>, Sb2O<sub>3</sub>, B-2 O<sub>3</sub>, Cr2O<sub>3</sub>, PbO, TiO<sub>2</sub>, SiO<sub>2</sub>, SnO<sub>2</sub>, Ta 2O<sub>5</sub>, GeO<sub>2</sub>, BaO, SrO, It has the configuration of consisting of oxide film containing the artificial oxides which heat-treated the range of 350 degrees C - 700 degrees C into the mixture which consists of Y2O<sub>3</sub>, Pr2O<sub>3</sub>, and at least two oxides in CoO and MnO, and were obtained into it.

[0019] In order to attain said object, further again the zinc-oxide system porcelain laminated material of

this invention MnO, CoO, Fe<sub>2</sub>O<sub>3</sub>, NiO and MgO, aluminum<sub>2</sub>O<sub>3</sub>, and the zinc-oxide system porcelain containing at least one oxide in BeO, Bi<sub>2</sub>O<sub>3</sub>, Sb<sub>2</sub>O<sub>3</sub>, B-2s Cr [ O<sub>3</sub> and ]<sub>2</sub>O<sub>3</sub>, PbO, TiO<sub>2</sub>, SiO<sub>2</sub>, SnO<sub>2</sub> and Ta<sub>2</sub>O<sub>5</sub>, GeO<sub>2</sub>, BaO, It has the configuration of coming to carry out the laminating of the oxide film containing SrO, Y<sub>2</sub>O<sub>3</sub>, Pr<sub>2</sub>O<sub>3</sub>, and at least two oxides in CoO and MnO by turns.

[0020] In the above-mentioned zinc-oxide system porcelain laminated material the oxide film Moreover, Bi<sub>2</sub>O<sub>3</sub>, Sb<sub>2</sub>O<sub>3</sub>, B-2 O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>, PbO, TiO<sub>2</sub>, SiO<sub>2</sub>, SnO<sub>2</sub>, Ta<sub>2</sub>O<sub>5</sub>, GeO<sub>2</sub>, BaO, SrO, It has the configuration of consisting of oxide film containing the artificial oxides which heat-treated the range of 350 degrees C - 700 degrees C into the mixture which consists of Y<sub>2</sub>O<sub>3</sub>, Pr<sub>2</sub>O<sub>3</sub>, and at least two oxides in CoO and MnO, and were obtained into it.

[0021] In order to attain said object, next, the manufacture approach of the zinc-oxide system porcelain laminated material of this invention The process which mixes and casts [ add and ] MnO, CoO, Fe<sub>2</sub>O<sub>3</sub>, NiO and MgO, aluminum<sub>2</sub>O<sub>3</sub>, and at least one oxide in BeO, sinters them to ZnO fine particles, and obtains zinc-oxide system porcelain, Bi<sub>2</sub>O<sub>3</sub>, Sb<sub>2</sub>O<sub>3</sub>, B-2s Cr [ O<sub>3</sub> and ]<sub>2</sub>O<sub>3</sub>, PbO, TiO<sub>2</sub>, SiO<sub>2</sub>, SnO<sub>2</sub> and Ta<sub>2</sub>O<sub>5</sub>, GeO<sub>2</sub>, BaO, The process which creates the artificial oxides which heat-treated the range of 350 degrees C - 700 degrees C into the mixture which consists of SrO, Y<sub>2</sub>O<sub>3</sub>, Pr<sub>2</sub>O<sub>3</sub>, and at least two oxides in CoO and MnO, It has the configuration of containing the process which forms the oxide film containing said artificial oxides on said zinc-oxide system porcelain, and the process which carries out the laminating of said zinc-oxide system porcelain through the aforementioned oxide film.

[0022] Next, in this invention, it has the configuration that the zinc oxide system porcelain laminated material in which the electrode was formed is a varistor. It is desirable to zinc-oxide system porcelain laminated material and really have calcinated the electrode in said varistor.

[0023]

[Embodiment of the Invention] The zinc-oxide system porcelain laminated material which heat-treated by arranging the oxide film which forms the liquid phase in the porcelain community of two zinc-oxide system porcelain at an elevated temperature consists of this inventions. And a varistor will be obtained if an electrode is formed in this. What was obtained in this way belongs to an interface barrier mold zinc oxide varistor.

[0024] In the conventional interface barrier mold zinc oxide varistor, the bisumuth oxide of a zinc oxide, the transition-metals oxide contributed to interface-state-density formation, and a solution layer formation object etc. was mixed, cast and calcinated, the electrode was attached, and the varistor had been obtained. In the varistor obtained in this way, interface state density is formed over all the zinc oxide particle communities, and each interface has the barrier of a double shot key mold.

[0025] The zinc-oxide system porcelain which constitutes the zinc-oxide system porcelain laminated material of this invention is sintered to high density, and the liquid phase generated even if it heat-treats on two zinc-oxide system porcelain communities by arranging the oxide film in connection with liquid phase formation on the occasion of elevated-temperature heat treatment is adjusted to the grain boundary of the zinc-oxide particle in zinc-oxide system porcelain, and a zinc-oxide particle so that it may not be spread. and heat treatment -- facing -- the liquid phase was formed only in two zinc-oxide system porcelain communities, and only by there having been carrier beam zinc-oxide system porcelain laminated material along the field of each zinc-oxide system porcelain about heat treatment, interface state density should be formed The zinc-oxide system porcelain with a high consistency casts mixture, such as a zinc oxide and an iron-group transition-metals oxide, and is calcinated and created. Baking of zinc-oxide system porcelain is faced. In order to make a high consistency have, a raw material is adjusted, and it calcinates at an elevated temperature, or CIP molding is carried out and it is calcinated. In order to raise a consistency furthermore, it calcinates by hot pressing, or performing HIP processing is performed. In order to improve junction of a zinc-oxide system porcelain community, grind the front face of each zinc-oxide system porcelain, a flat field is made to have, it heat-treats by joining the zinc-oxide system porcelain to which two polishes were given through the oxide film in connection with liquid phase formation, and zinc-oxide system porcelain laminated material is obtained.

[0026] It analyzed in detail about work of the oxide film in connection with the liquid phase formation which reacts on the other hand at ZnO which is also the principal component of zinc-oxide system

porcelain, and this and an elevated temperature. consequently,  $\text{Sb}_2\text{O}_3$  and  $\text{SnO}_2$  etc. -- if it is added in the oxide film in connection with liquid phase formation while it has been independently unreacted, these will be sublimated at quite low temperature, will adhere to the front face of zinc-oxide system porcelain, will carry out solid phase reaction to a zinc oxide, will form the compound thin film of firm solid phase, and will bar the reaction of the zinc oxide and the liquid phase which should occur at an elevated temperature. Since  $\text{Sb}_2\text{O}_3$ ,  $\text{SnO}_2$ , etc. are important matter in order to improve the dependability of a varistor, it is desirable to make it contain in the oxide film in connection with liquid phase formation. \*\* -- when like, it is made to react between the matter in the oxide film beforehand, and if it is made to contain in the oxide film in connection with liquid phase formation, each component will work effectively. If add heat treatment beforehand, a part of  $\text{Sb}_2\text{O}_3$  which will be added if an example is raised, and  $\text{Bi}_2\text{O}_3$  added are made to react by solid phase and the synthetic powder of  $\text{Bi}_2\text{O}_3$  and  $\text{Sb}_2\text{O}_3$  is added, sublimation of  $\text{Sb}_2\text{O}_3$  will be controlled in the case of heat treatment, and the effective liquid phase will be formed.

[0027] The varistor using the barrier of the double shot key mold which consists of one pair of layers produced in a zinc oxide system porcelain interface shows the stable I-V property which was excellent in the nonlinear resistive characteristic. Since it is the varistor which consists of barrier of one pair of double shot key molds, it starts, and an electrical potential difference becomes settled mostly with about 3 V. In the porcelain interface barrier mold zinc oxide varistor manufactured in this way . in which a depletion layer is formed in accordance with a zinc oxide system porcelain interface, and the barrier of a double shot key mold is formed, since this barrier exists If a current does not flow, but an electrical potential difference is called voltage at reference current, it starts and an electrical potential difference is reached in the beginning even if it forms an electrode in a sintered compact and carries out the seal of approval of the electrical potential difference to it, a current will begin to flow rapidly. . from which the low-battery varistor of low electrostatic capacity is obtained by narrowing area of a barrier part by the varistor in which the so-called varistor property appears, and. Starting The low-battery varistor of necessary low electrostatic capacity can be further obtained combining these varistors.

[0028] . to which three kinds of things are mainly in the porcelain community barrier mold zinc oxide varistor of this invention -- that first thing heat-treats by arranging other zinc oxide system porcelain through the oxide film in connection with liquid phase formation to one place of the front face of zinc oxide system porcelain, obtains zinc oxide system porcelain laminated material, and then forms two ohmic electrodes in this zinc oxide system porcelain laminated material. That second thing heat-treats by arranging other zinc-oxide system porcelain through the oxide film in connection with liquid phase formation to two places of the front face of zinc-oxide system porcelain, obtains zinc-oxide system porcelain laminated material, and then forms two ohmic electrodes in this zinc-oxide system porcelain laminated material. The third thing carries out the laminating of zinc-oxide system porcelain and the oxide film in connection with liquid phase formation by turns, heat-treats to the layered product, obtains zinc-oxide system porcelain laminated material, and comes to form an ohmic electrode.

[0029]

[Example] This invention is explained still more concretely using an example below.

[0030] (Example 1) The powder of  $\text{ZnO}$  and the powder of  $\text{Co}_3\text{O}_4$ , and  $\text{MnO}_2$  and  $\text{NiO}$  are mixed so that it may be set to 81.38 g:0.954 g:0.414 g:0.383 g by the weight ratio, an aluminium nitrate is converted into aluminum  $2\text{O}_3$  in the form of a water solution, and it is 1.51 mg. It added.

0.5mmx0.5mm after casting this mixed powder and giving hotpress baking of 1 hour at 1300 degrees C under an atmospheric-air ambient atmosphere, It cuts and grinds in sample size with a thickness of 0.3mm, Two zinc-oxide system porcelain was obtained.

[0031] Next, it ground, after mixing  $\text{Bi}_2\text{O}_3$  and  $\text{SnO}_2$  by the ratio of 356.8 g:30.14 g and performing heat treatment of 2 hours at 550 degrees C, and the synthetic powder of  $\text{Bi}_2\text{O}_3$  and  $\text{SnO}_2$  was obtained. Moreover, it is 111.5 g about  $\text{Bi}_2\text{O}_3$  and B-2  $\text{O}_3$  . : It ground, after mixing by the ratio of 8.7 g and performing heat treatment of 2 hours at 400 degrees C, and the synthetic powder of  $\text{Bi}_2\text{O}_3$  and B-2  $\text{O}_3$  was obtained. Synthetic powder of  $\text{Bi}_2\text{O}_3$  and  $\text{SnO}_2$  which were obtained in this way Synthetic powder of 50g,  $\text{Bi}_2\text{O}_3$ , and B-2  $\text{O}_3$  It mixed at a rate of 10g, water was added and pasted, and the oxide paste

was obtained.

[0032] Said oxide paste was applied to one side of the zinc-oxide system porcelain which is the above, and was made and obtained, other zinc-oxide system porcelain was carried and pressurized on it, temperature up was carried out with the programming rate of 50 degrees C/hour among atmospheric air, and after holding at 900 degrees C for 1 hour, the tabular zinc-oxide system porcelain laminated material which lowers the temperature at 50 degrees C/hour in temperature fall rate, and uses a zinc oxide as a principal component was obtained.

[0033] Next, the creation approach of a zinc oxide varistor is explained, referring to drawing 1. drawing 1 -- both sides of the zinc-oxide system porcelain laminated material of this invention -- Ore -- it is the outline perspective view of the zinc-oxide varistor 10 which formed the Mick silver electrode, and attached and obtained lead wire with the pewter to each electrode. Two zinc-oxide system porcelain 11 and 12 has countered through porcelain \*\*\*\* 13 which consists of oxide film. both sides of the zinc-oxide system porcelain laminated material which is the above, and was made and obtained -- Ore -- the Mick silver electrodes 14 and 15 are formed, lead wire 16 and 17 is attached to each electrode with a pewter, and an epoxy resin (not entered by a diagram) is painted for the structures other than lead wire.

[0034] Thus, the electrical property of the obtained zinc oxide varistor was evaluated. as an early electrical property -- starting -- electrical-potential-difference V1mA, and (electrical potential difference between the ends children when passing a 1mA current) alpha with a nonlinear resistance characteristic of 0.1mA 1mA (value calculated using V1mA and V0.1mA) Electrostatic capacity (1 kHz) and tandelta were measured (in the publication of still the following, alpha with a nonlinear resistance characteristic of 0.1mA 1mA may only be called alpha value for short). Surge absorptance becomes large, so that a nonlinear resistance characteristic is large. Moreover, the dependability over a direct-current load was evaluated. In the inside of a 80-degree C elevated-temperature ambient atmosphere It is a 1.25mW direct-current load 500 Time amount impression was carried out and varistor standup electrical-potential-difference V1mA rate-of-change \*\*V1 mA/V1mA (rate of a direct-current change of load) was measured. The electrical property of a zinc oxide varistor is stable, and it is shown that it is reliable, so that varistor standup electrical-potential-difference V1mA rate-of-change \*\*V1 mA/V1mA is small. Furthermore, the dependability over a surge was evaluated. Varistor standup electrical-potential-difference V1mA rate-of-change \*\*V1 mA/V1mA (surge rate of change) by 10 times impression of the pulse of 8x 20microsec and 5Amp was measured. The presentation of a sample is shown in a table 1 and the assessment result of an electrical property is shown in a table 2. The electrical property of a zinc oxide varistor is stable, and it is shown that it is reliable, so that the value of surge rate of change is small. All show that rate of change is reliable at 5% or less. In addition, the numeric value which shows the assessment result of an electrical property showed the minimum value and maximum in a lot.

[0035]

[A table 1]

酸化亜鉛系磁器材料 (wt ratio)					酸化物膜材料 (wt ratio)			
ZnO	Co <sub>3</sub> O <sub>4</sub>	MnO <sub>2</sub>	NiO	Al <sub>2</sub> O <sub>3</sub>	Bi <sub>2</sub> O <sub>3</sub>	SnO <sub>2</sub>	Bi <sub>2</sub> O <sub>3</sub>	B <sub>2</sub> O <sub>3</sub>
81.38g	0.954g	0.414g	0.383g	1.51mg	356.8g	30.14g	111.5g	8.7g
					50g		10g	

[0036]

[A table 2]

静電容量 (pF)	tan δ (%)	V1mA/mm (V)	0.1mA α 1mA	直流負荷変化率(%) ΔV1mA/V1mA	サージ変化率(%) ΔV1mA/V1mA
71-90	2.3-2.7	3.05-3.2	15-19	-2--4	-1--3

[0037] The zinc oxide varistor using the zinc oxide system porcelain laminated material of this example had small electrostatic capacity, and its nonlinear resistive characteristic was good, it started also to the surge also to the direct-current load of long duration, the absolute value of electrical-potential-difference



V1mA rate of change (\*\*V1 mA/V1mA) is 5% or less, and dependability was superior to a table 1 and a table 2. Moreover, the variation in the electrical property in a lot was also small as shown in a table 2. Although not shown in a table 2, when the zinc oxide varistor was created using the zinc oxide system porcelain laminated material of this example, the variation of a lot-to-lot electrical property as well as the variation in the electrical property in a lot was small.

[0038] (Example 2) Next, example Zinc-oxide system porcelain was created by the approach of 1 and resemblance. The powder of ZnO and the powder of Co<sub>3</sub>O<sub>4</sub>, and MnO<sub>2</sub> and MgO are mixed so that it may be set to 81.38 g:0.954 g:0.414 g:0.806 g by the weight ratio, an aluminium nitrate is converted into aluminum 2O<sub>3</sub> in the form of a water solution, and it is 1.02mg. It added. After casting this mixed powder and giving hotpress baking of 1 hour at 1300 degrees C under an atmospheric-air ambient atmosphere, two pieces and one 5 mmx1 mmx0.3mm zinc-oxide system porcelain were cut, the zinc-oxide system porcelain of the size of 0.5mmx0.5mm and thickness 0.3 mm was ground, and zinc-oxide system porcelain was obtained.

[0039] Next, it ground, after mixing Bi<sub>2</sub>O<sub>3</sub> and Sb<sub>2</sub>O<sub>3</sub> by the ratio of 139.8 g:58.3 g and performing heat treatment of 2 hours at 550 degrees C, and the synthetic powder of Bi<sub>2</sub>O<sub>3</sub> and Sb<sub>2</sub>O<sub>3</sub> was obtained. Moreover, Bi<sub>2</sub>O<sub>3</sub> It is 111.5 g about B-2 O<sub>3</sub>. : It grinds, after mixing by the ratio of 8.7 g and performing heat treatment of 2 hours at 400 degrees C, and it is Bi<sub>2</sub>O<sub>3</sub>. Synthetic powder with B-2 O<sub>3</sub> was obtained. It is 111.5 g about Bi<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub> further again. : It ground, after mixing by the ratio of 38.0 g and performing heat treatment of 2 hours at 550 degrees C, and the synthetic powder of Bi<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub> was obtained. Synthetic powder of Bi<sub>2</sub>O<sub>3</sub> obtained in this way and Sb<sub>2</sub>O<sub>3</sub> 50 g and Bi<sub>2</sub>O<sub>3</sub> Synthetic powder with B-2 O<sub>3</sub> Synthetic powder of 10 g, Bi<sub>2</sub>O<sub>3</sub>, and Cr<sub>2</sub>O<sub>3</sub> It mixed at a rate of 10 g, water was added and pasted, and the oxide paste was obtained.

[0040] Next, the creation approach of a zinc oxide varistor is explained, referring to drawing 2.

Drawing 2 is the outline sectional view of the zinc oxide varistor 20 which formed the electrode in the zinc oxide system porcelain laminated material of this invention, and attached and obtained lead wire. After having arranged zinc-oxide system porcelain, carrying out temperature up with the programming rate of 50 degrees C/hour among atmospheric air through the oxide film which applied said oxide paste and was obtained on the two top face of the zinc-oxide system porcelain which is the above, and was made and obtained and holding at 930 degrees C for 1 hour, the temperature was lowered at 50 degrees C/hour in temperature fall rate, and the zinc-oxide system porcelain laminated material of this invention was obtained. On both sides of porcelain \*\*\*\* 22 and 23 which consists of oxide film, the laminating of the zinc-oxide system porcelain 24 and 25 is carried out, and lead wire 28 and 29 is attached to two electrodes 26 and 27 with the pewter on each.

[0041] Thus, the approach of an example 1 and resemblance estimated the electrical property of the obtained zinc oxide varistor. As an early electrical property, it is sink standup electrical-potential-difference V1mA about a current. And electrostatic capacity (1 kHz) and tandelta, Nonlinear resistance characteristic alpha It measured. By the direct-current load test 2.5 mW 500 The rate of change when carrying out time amount impression was searched for. Moreover, varistor standup electrical-potential-difference V1mA rate-of-change \*\*V1 mA/V1mA (surge rate of change) by 10 times impression of the pulse of 8x 20microsec and 5Amp was measured. The presentation of a sample is shown in a table 3 and the assessment result of an electrical property is shown in a table 4. The electrical property of a zinc oxide varistor is stable, and it is shown that it is reliable, so that the value of surge rate of change is small. All show that rate of change is reliable at 5% or less. In addition, the numeric value which shows the assessment result of an electrical property showed the minimum value and maximum in a lot.

[0042]

[A table 3]

酸化亜鉛系磁器材料 (wt raitio)					酸化物膜材料 (wt raitio)					
ZnO	Co <sub>3</sub> O <sub>4</sub>	MnO <sub>2</sub>	MgO	Al <sub>2</sub> O <sub>3</sub>	Bi <sub>2</sub> O <sub>3</sub>	Sb <sub>2</sub> O <sub>3</sub>	Bi <sub>2</sub> O <sub>3</sub>	B <sub>2</sub> O <sub>3</sub>	Bi <sub>2</sub> O <sub>3</sub>	Cr <sub>2</sub> O <sub>3</sub>
81.38g	0.954g	0.414g	0.806g	1.02mg	356.8g	30.14g	111.5g	8.7g	111.5g	38.0g
					50g		10g			10g



[0043]

[A table 4]

静電容量 (pF)	$\tan \delta$ (%)	V1mA/mm (V)	U. 1mA $\alpha$ 1mA	直流負荷変化率(%) $\Delta V1mA/V1mA$	サージ変化率(%) $\Delta V1mA/V1mA$
35-45	2.2-3.0	5.9-6.2	16-19	-1--3	0--2

[0044] The zinc oxide varistor using the zinc oxide system porcelain of this example had small electrostatic capacity, and its nonlinear resistive characteristic was good, it started also to the surge also to the direct-current load of long duration, the absolute value of electrical-potential-difference V1mA rate of change (\*\*V1 mA/V1mA) is 5% or less, and dependability was superior to a table 3 and a table 4. Moreover, the variation in the electrical property in a lot was also small as shown in a table 4. Although not shown in a table 4, when the zinc oxide varistor was created using the zinc oxide system porcelain of this example, the variation of a lot-to-lot electrical property as well as the variation in the electrical property in a lot was small.

[0045] (Example 3) The powder of ZnO and the powder of Co<sub>3</sub>O<sub>4</sub>, and MnO<sub>2</sub> and BeO are mixed so that it may be set to 81.38 g:0.954 g:0.414 g:0.500 g by the weight ratio, an aluminium nitrate is converted into aluminum 2O<sub>3</sub> in the form of a water solution, and it is 0.76 mg. It added.

0.5mmx0.5mm after carrying out CIP molding of this mixed powder and giving baking of 3 hours at 1400 degrees C under an atmospheric-air ambient atmosphere, It cut and ground in the sample size of thickness 0.3 mm, and zinc-oxide system porcelain was obtained.

[0046] Next, it ground, after mixing Bi<sub>2</sub>O<sub>3</sub>, Sb<sub>2</sub>O<sub>3</sub>, and TiO<sub>2</sub> by the ratio of 178.4 g:21.9 g:20.0 g and performing heat treatment of 2 hours at 550 degrees C, and the synthetic powder of Bi<sub>2</sub>O<sub>3</sub>, Sb<sub>2</sub>O<sub>3</sub>, and TiO<sub>2</sub> was obtained. Moreover, it is 111.5 g about Bi<sub>2</sub>O<sub>3</sub> and B-2 O<sub>3</sub>. : It ground, after mixing by the ratio of 8.7 g and performing heat treatment of 2 hours at 400 degrees C, and the synthetic powder of Bi<sub>2</sub>O<sub>3</sub> and B-2 O<sub>3</sub> was obtained. Furthermore, it is 111.5 g about Bi<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub>. : It ground, after mixing by the ratio of 38.0 g and performing heat treatment of 2 hours at 550 degrees C, and the synthetic powder of Bi<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub> was obtained. The synthetic powder of 1.0g, Bi<sub>2</sub>O<sub>3</sub>, and Cr<sub>2</sub>O<sub>3</sub> was mixed for 5.0g of synthetic powder of Bi<sub>2</sub>O<sub>3</sub>, Sb<sub>2</sub>O<sub>3</sub>, and TiO<sub>2</sub> which were obtained in this way, and the synthetic powder of Bi<sub>2</sub>O<sub>3</sub> and B-2 O<sub>3</sub> at a rate of 1.0g, water was added and pasted, and the oxide paste was obtained.

[0047] Next, the creation approach of a zinc oxide varistor is explained, referring to drawing 3. drawing 3 -- both sides of the zinc-oxide system porcelain laminated material of this invention -- Ore -- it is the outline sectional view of the zinc-oxide varistor 30 which formed the Mick silver electrode, and attached and obtained lead wire with the pewter to each electrode. The laminating of the three oxide film by four zinc-oxide system porcelain which is the above, and was made and obtained, and said oxide paste is carried out by turns. . which obtained the zinc-oxide system porcelain laminated material of the shape of a laminating which carries out temperature up with the programming rate of 50 degrees C/hour among atmospheric air, lowers the temperature at 50 degrees C/hour in temperature fall rate, and uses a zinc oxide as a principal component after holding at 870 degrees C for 1 hour The laminating of the zinc-oxide system porcelain 31 and porcelain \*\*\*\* 32 which consists of oxide film is carried out by turns among drawing. Next, after forming the ohmic electrodes 33 and 34 in both sides of this zinc-oxide system porcelain laminated material and attaching lead wire 35 and 36 to an electrode with a pewter, the zinc-oxide varistor is formed by carrying out the epoxy resin paint of the structures other than lead wire.

[0048] Thus, the approach of an example 1 and resemblance estimated the electrical property of the obtained zinc oxide varistor. By the direct-current load test 3.5 mW 500 The rate of change when carrying out time amount impression was searched for. Moreover, varistor standup electrical-potential-difference V1mA rate-of-change \*\*V1 mA/V1mA (surge rate of change) by 10 times impression of the pulse of 8x 20microsec and 5Amp was measured. The presentation of a sample is shown in a table 5 and the assessment result of an electrical property is shown in a table 6. The electrical property of a zinc oxide varistor is stable, and it is shown that it is reliable, so that the value of surge rate of change is

small. All show that rate of change is reliable at 5% or less. In addition, the numeric value which shows the assessment result of an electrical property showed the minimum value and maximum in a lot.

[0049]

[A table 5]

酸化物系セラミックス材料 (wt ratio)					酸化物系材料 (wt ratio)						
ZnO	Co <sub>3</sub> O <sub>4</sub>	MnO <sub>2</sub>	BaO	Al <sub>2</sub> O <sub>3</sub>	Bi <sub>2</sub> O <sub>3</sub>	Sb <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	Bi <sub>2</sub> O <sub>3</sub>	B <sub>2</sub> O <sub>3</sub>	Bi <sub>2</sub> O <sub>3</sub>	Cr <sub>2</sub> O <sub>3</sub>
81.38g	0.954g	0.414g	0.500g	0.76mg	178.4g	21.9g	20g	111.5g	8.7g	111.5g	38.0g
					50g		10g		10g		

[0050]

[A table 6]

静電容量 (pF)	tan δ (%)	V1mA/mm (V)	0.1mA α 1mA	直流負荷変化率(%) ΔV1mA/V1mA	サージ変化率(%) ΔV1mA/V1mA
26-32	2.5-2.8	9.1-9.5	14-18	-1--4	-2--3

[0051] The nonlinear resistive characteristic was good and started also to the surge also to the direct-current load of long duration, the absolute value of electrical-potential-difference V1mA rate of change (\*\*V1 mA/V1mA) is 5% or less, and the zinc oxide varistor using the zinc oxide system porcelain laminated material of this example excelled a table 5 and a table 6 in dependability. Moreover, the variation in the electrical property in a lot was also small as shown in a table 6. Although not shown in a table 6, when the zinc oxide varistor was created using the zinc oxide system porcelain of this example, the variation of a lot-to-lot electrical property as well as the variation in the electrical property in a lot was small.

[0052]

[Effect of the Invention] As explained using three examples above, this invention offers the zinc oxide varistor for low batteries which was excellent in an electrical property and dependability, such as a nonlinear resistive characteristic, with low electrostatic capacity by the high yield. If digitization of an electronic circuitry progresses, the noise of a high frequency will occur. . from which clearance of the noise of a high frequency serves as pressing need with the digitized various electronic instruments In the circuit especially using a semi-conductor . asked for the varistor for low batteries 10 volts or less for a standup electrical potential difference Although surge absorptance was excellent in the conventional grain boundary barrier mold, in the object for low batteries, the number of the inter-electrode barrier of the sintered compact of a component is uncontrollable. The variation in the value of a standup electrical potential difference was large, and utilization was difficult. Although the easy silver of operation was used as an electrode material in this invention in the . example which the barrier of a double shot key mold was formed in porcelain \*\*\*\* inserted with the zinc oxide system porcelain of the high consistency of two pieces, made small area of . which obtained the low-battery varistor by attaching an electrode, and porcelain \*\*\*\*, and obtained the zinc oxide varistor for low batteries with low electrostatic capacity, the metal and alloy which do not oxidize in an oxidizing atmosphere can be used. Moreover, although used in the example combining the mixed powder which heat-treated by having chosen 2-3 sorts in Bi 2O<sub>3</sub>, Sb<sub>2</sub>O<sub>3</sub>, B-2s Cr [ O<sub>3</sub> and ] 2O<sub>3</sub>, and TiO<sub>2</sub> and SnO<sub>2</sub> as an ingredient which forms porcelain \*\*\*\*, and having mixed, or performed those heat treatments PbO, SiO<sub>2</sub>, Ta 2O<sub>5</sub>, GeO<sub>2</sub>, BaO and SrO, Y<sub>2</sub>O<sub>3</sub>, Pr<sub>2</sub>O<sub>3</sub>, CoO, If the leakage current is small when it chooses out of from while also including MnO, the varistor which is characteristic, respectively -- excel in nonlinearity in the high current region, or it is suitable for electrode formation at low temperature -- can be obtained.

[Translation done.]